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GROWTH, CHARACTERIZATION, AND POTENTIAL APPLICATIONS OF PERIODIC CARBON NANOTUBE ARRAYS

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ABSTRACT

Aligned carbon nanotubes have been made by plasma enhanced chemical vapor deposition. Based on the technique used to prepare the catalyst dots, aligned arrays of carbon nanotubes could be made either without or with periodicity. In this paper, we report the development of carbon nanotubes arrays both without and with periodicity using cheap and scalable technologies. The periodic arrays show very interesting optical properties.

1. INTRODUCTION

Large arrays of well-aligned carbon nanotubes are first made possible on substrates in 1998 by plasma enhanced chemical deposition (PECVD) [1,2] in which the diameter and length of each carbon nanotube are under control, but not the growth angle, location, nor the spacing between them. Soon after, the titled growth has been achieved by controlling the plasma direction using the same growth technique [3]. Almost at the same time, the control of location and spacing of the nanotubes have been accomplished using electron beam (e-beam) lithography to pattern the nickel dots first at where they are needed and then to grow the carbon nanotubes using the same growth technique [4,5]. However, e-beam is not possible to be commercialized for large scale. Therefore, alternative cheap and scalable technique is sought. Fortunately, the catalytic dots have been fabricated by electrochemistry and excellent aligned carbon nanotubes arrays have been grown [6]. Due to the nature of electrochemistry, the control on location of each nanotube is lacking. For applications that do not require the pre-determined location of each nanotube such as regular electron source, the arrays grown using the dots by electrochemistry is good enough. However, for applications that do require the pre-determined location of each nanotube such as microscopic probing tips, nanophotonics, etc., the control of location of each nanotube is crucial. Recently, we have been successful to grow large arrays of carbon nanotubes with diameter, length, location, and spacing under control by a simple and scalable technique, nanosphere lithography [7, 8]. Since the very first report on large arrays of well-aligned carbon nanotubes, numerous papers have used the same or a slightly modified technique to grow aligned carbon nanotube arrays by either DC or microvave plasma CVD [9-19].

2. EXPERIMENTAL

The catalytic dots have been prepared by four techniques: magnetron sputtering, e-beam lithography, pulse current electrochemistry, and nanosphere lithography. The growth was accomplished by PECVD. The gases used are acetylene and ammonia that provides the carbon source and catalytic effect respectively. Scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to characterize the arrays.

3. RESULTS

3.1 Aligned Growth of Carbon Nanotubes on Sputtered Ni Films

Fig. 1 shows the SEM images of the arrays of carbon nanotubes grown on glass substrates by plasma enhanced chemical vapor deposition [1]. They clearly show the excellent alignment with the glass substrate. In order to measure the alignment, diameter, and length of the carbon nanotubes, part of the sample was scraped as shown. For this particular sample, the tubes are about 20 μm long. For diameter estimate, higher magnification SEM exam was carried out.

Fig. 2 shows SEM images of the aligned carbon nanotube arrays in higher magnifications. Clearly, nanotubes with different diameters have been produced.

The diameters are controlled by the thickness of the catalytic Ni layer: the thinner the Ni, the smaller the nanotubes. For a thickness of 15 nm, nanotubes are about 50 nm in diameter as shown in Fig. 2A, whereas a 40 nm thick Ni yielded nanotubes of about 250 nm in diameter as shown in Fig. 2B. Further reduction of Ni thickness has yielded nanotubes with diameters in the range of 10 – 25 nm, but without excellent alignment if the length is more than a few μm.

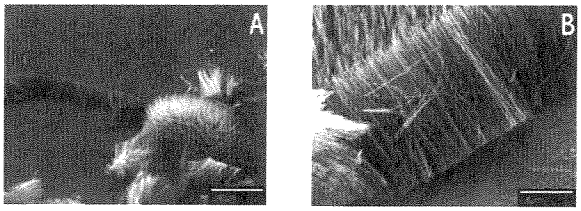

Figure 1. SEM images of aligned carbon nanotubes. A) low magnification to show the alignment over large area, B) medium magnification to show the length of the nanotubes.

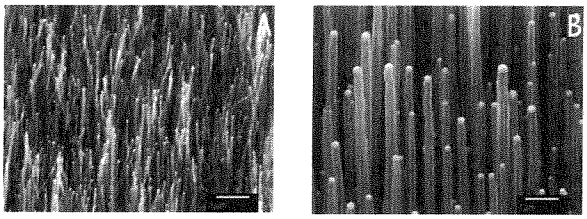

Figure 2. SEM images of carbon nanotube arrays grown with different thickness of Ni layers. A) 15 nm thick Ni, B) 40 nm thick Ni.

3.2 Aligned Growth of Carbon Nanotubes on Ni Dots Made by e-beam Lithography

For e-beam lithography, thin film nickel (Ni) patterns were fabricated on a p-type boron doped (100) silicon substrate. Ni layer of 15 nm was deposited by thermal evaporation. The patterned substrate was loaded into a PECVD system. The growth was carried out at the similar conditions as above.

Fig. 3 is a series of SEM micrographs showing the growth of single multiwall carbon nanotubes on each dot of an array of ~100 nm nickel dots. Figures 2a, 2c, 2e, and 2f were taken at an inclined angle, and Figures 2b and 2d are top views taken normal to the substrate. Figures 2a and 2b demonstrate selective growth of the carbon structures on the multiply repeated array patterns. The grown structures accurately reflect the spacing and periodicity of the lithographically patterned Ni dots. Figures 2c and 2d were taken at a higher magnification and show the repeated array pattern where the nanotubes are spaced either 2 μm apart (left) or 1 μm apart (right). Significant variation in the height (0.1 to 5 μm) of the grown bundles is observed, with no apparent relationship between height and spatial position. We note that even though the heights are different by more than a factor of 10, the base diameters are approximately uniform (~ 150 nm). Figure 2f shows the growth on a grid of Ni dots spaced 5 μm apart, indicating little dependence of growth on spacing (for spacing > 1 μm). The reason for such aligned growth of single carbon nanotubes in our system is due to the plasma, which is also used widely by others since our initial report [1].

Soon after, we were successful on obtaining patterns with more uniform length as shown in Fig. 4. Each nanotube has a sharp tip with radius of about 2-3 nm that may be very useful for high current field emission applications. Unfortunately, the nice patterns grown using e-beam lithography is only good for concept proving. In the next, we present a cheap way for fabricating arrays with spacing, but not location, controlled: electrochemistry.

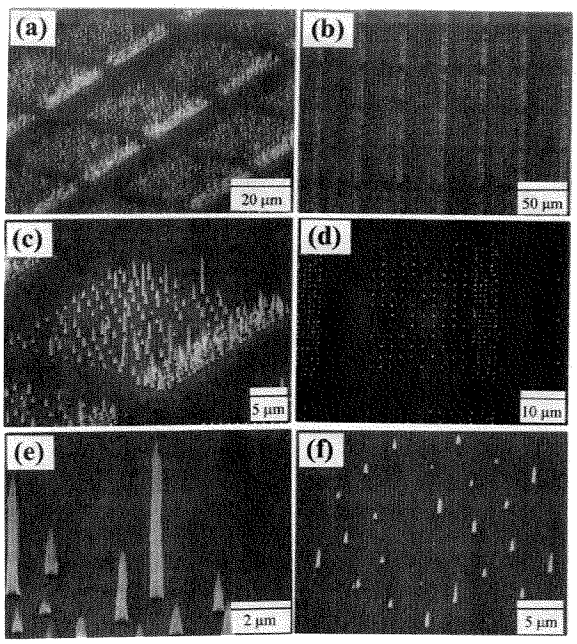

Figure 3. A series of SEM micrographs from different viewing angles showing growth of carbon nanotube obelisks on an array of submicron nickel dots. (a) An inclined view of a repeated array pattern. (b) A top (normal) view of a repeated array pattern. (c) An inclined view of one array pattern. (d) A top (normal) view of one array pattern. The initial Ni dots (and subsequently the grown carbon structures) are spaced either 2 μm apart (left) or 1 μm apart (right). (e) A magnified view along the edge of one pattern. A sharp, tapered tip is evident. (f) An inclined view of carbon obelisks grown on nickel dots separated by 5 μm.

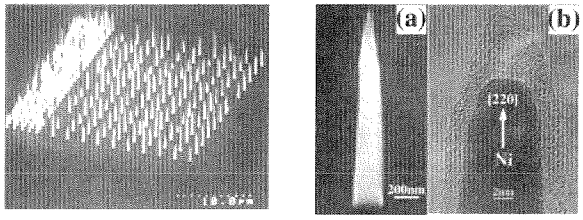

Figure 4. SEM and TEM images of carbon nanotube arrays.

3.3. Growth of Aligned Carbon Nanotubes with Spacing Controlled by Electrochemistry

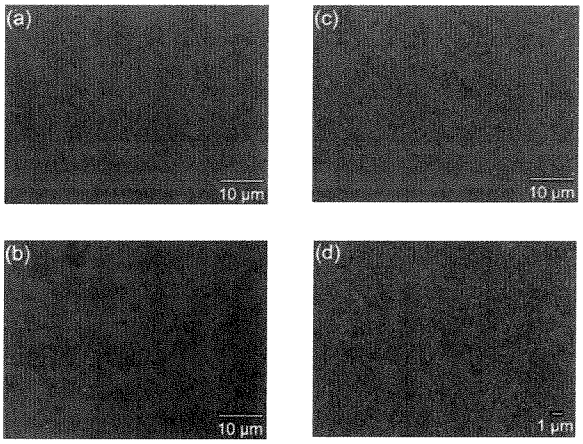

Figure 5. SEM images of Ni nanoparticles deposited electrochemically with site density of (a) $7.5x10^5$ cm^{-2}, (b) $2x10^6$ cm^{-2}, (c) $2x10^7$ cm^{-2}, and (d) $3x10^8$ cm^{-2}.

Fig. 5 shows the different nucleation site densities of the Ni nanoparticles from about $7.5x10^5$ cm^{-2} to $3x10^8$ cm^{-2} by electrochemistry. The white dots shown in the pictures were the Ni nanoparticles that had been confirmed by Energy Dispersive X-ray Spectroscopy (EDX). Most particles had diameter from 100 nm to 200 nm with some nanoparticles smaller than 50 nm. The Ni nanoparticles were randomly located on the surface of the substrate.

Fig. 6 (a) to (e) shows the different site densities of CNTs grown from the electrodeposited Ni nanoparticles. The CNTs site densities of the samples were about $7.5x10^5$, $2.0x10^6$, $6.0x10^6$, $2.0x10^7$, and $3x10^8$ cm^{-2}, respectively. Fig. 6 (f) provides a closer look at one of the well-aligned CNTs.

3.4. Growth of Aligned Carbon Nanotube Arrays with Periodicity

Even though electrochemistry provided excellent control on site density, but could not produce Ni dots at the pre-determined locations. Fortunately, we have developed another technique, nanosphere lithography, to fulfill the goal. Fig. 7 shows the SEM images of the Ni dots made by nanolithography. Fig. 8 shows the nanotubes made from the dots shown in Fig. 7. Surprisingly, every sample is colorful (shown in Fig. 9) instead of being black as those without periodicity. The bright reflection of red, green, and blue light was recorded at three different angles from a white incident light, which demonstrates that such an array can be used as an optical filter.

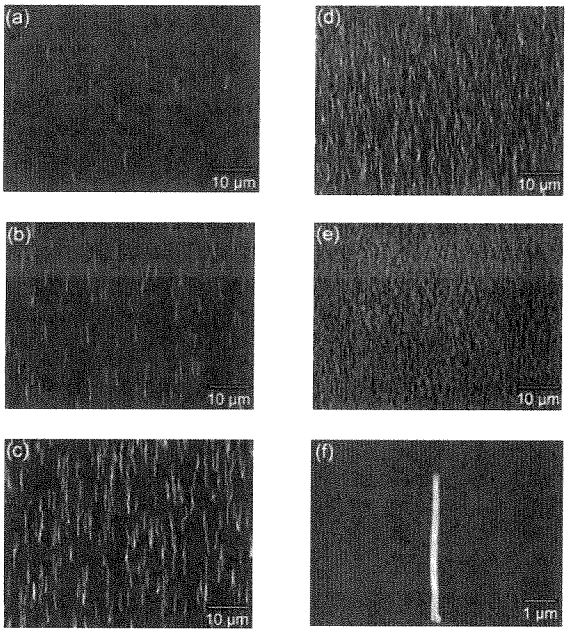

Figure 6. SEM images of aligned CNTs with site density of (a) $7.5x10^5$ cm^{-2}, (b) $2x10^6$ cm^{-2}, (c) $6x10^6$ cm^{-2}, (d) $2x10^7$ cm^{-2}, (e) $3x10^8$ cm^{-2}, and (f) a single standing CNT.

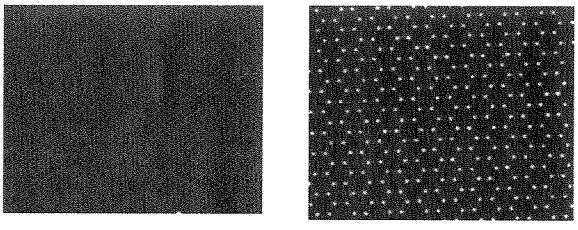

Figure 7. SEM images of Ni dots made by nanolithography in low (left) and medium (right) magnifications.

In addition to these straightforward diffraction effects, our arrays of nanotubes can act also as 2D photonic band gap crystals. It has been shown [20], that

periodic arrays of structures having dielectric constants (ε_a) different from the environment (ε_b), act on propagating photons not only by enforcing the Bragg scattering as discussed above, but also, in a complete analogy to the electron propagation in atomic crystals, lead to the opening of energy (frequency) gaps at the Bragg reflection points, i.e. at the Brillouin zone boundaries. If such gaps occur at all propagation directions of the photon (or electron), an absolute gap exists in the photonic spectrum, which in the case of the photonic crystal leads to a total reflection of light in this frequency band. It has been shown [21, 22] that a honeycomb array of rods, with large dielectric constant, embedded in a material with low dielectric constant, produces photonic band structure with absolute gaps at low fillings. This was later confirmed by an experiment in the microwave frequency range [23] in a perfect agreement with the theory. It was also shown, that a simple size scaling ($\omega \sim 1/a$) holds for the gaps, and therefore one can simply rescale the results of these papers to systems with different sizes, such as honeycomb arrays of nanotubes.

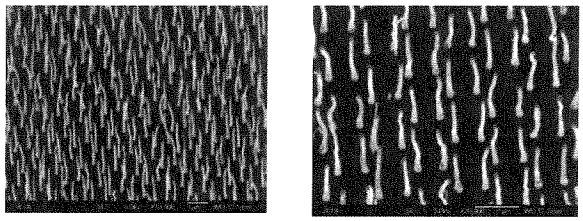

Figure 8. SEM images of low (left) and medium (right) magnifications of carbon nanotube arrays.

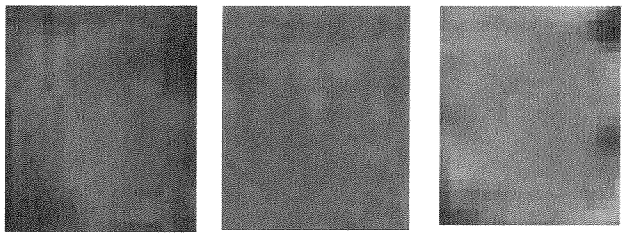

Figure 9. Bright diffraction colors of red, blue, and green.

Even though our nanotubes have dielectric constant that is different from that of the nanorods considered in Refs. 21-23, we can still directly employ results of these references to our arrays of nanotubes, after proper dielectric constants scaling. First we note that in the theory of Refs. 22 and 23, all the relative sizes of the gaps $\delta_i = |\Delta\omega_i/\omega_i|$ are approximately proportional to the Fourier components of the perturbation (dielectric constant inhomogeneity), which in turn, for a system with $\varepsilon_a > \varepsilon_b$, are proportional to $p = 1/\varepsilon_b - 1/\varepsilon_a$. Therefore we find that $\delta_i \sim p$. Since this is the only dependency on εa and εb in the gap equations, the results for various gaps obtained in Refs. 21 and 22 can be simply scaled (by using p) to obtain corresponding results for systems with different dielectric constants. Using this, we immediately show that the honeycomb array of our nanotubes obtained by using nanospheres of diameter 0.5 μm, should act as a 2D photonic band gap crystal with the gap at the radiation wavelength $\lambda \approx 0.5$ μm. Since our metallic nanotubes have $\varepsilon_a < 0$ in the visible frequency range (their plasma frequency is at 6.5 eV), this yields $p > 1$, and therefore the gap size is expected to be $\delta_2 > 15\%$. Note, that since the dielectric constant of nanotubes has also an imaginary part (losses), the gap does not imply a perfect reflection. The experimental effort to demonstrate the photonic band gap in our nanotube arrays is in progress.

We note, that the nanotubes can be coated for better control of the photonic crystal parameters. They can also be used as structural templates, to obtain nonmetallic photonic arrays, including nonmetallic 2D band gap crystals.

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CONCLUSIONS

Well-aligned carbon nanotube arrays without periodicity have been achieved on either Ni films made by magnetron sputtering or Ni dots made by electrochemical deposition, whereas the arrays with periodicity have been realized on either Ni dots made by e-beam lithography or on Ni dots made by nanosphere lithography. Obviously, the electrochemical deposition is much better than magnetron sputtering, and the nanosphere lithography is much better than e-beam lithography in the sense of both the cost and scalability. The large periodic arrays not only reflect and diffract light to show colors but also potentially is excellent photonic band gap crystals.